Microscopy with Single Atom Sensitivity for Solving Catalysis Problems

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Goal

Address fundamental problems in catalytic systems using a combination of Z-contrast STEM with single-atom sensitivity and density functional theory calculations.

Recent Progress

High Catalytic Activity from 1 nm Au clusters on TiO_2: The 0.7 Å diameter beam of the aberration-corrected, 300 kV scanning transmission electron microscope (STEM) at ORNL provides the highest sensitivity for imaging individual atoms. Nanometer-sized gold particles were deposited on a variety of supports (mesoporous titania, anatase, brookite, rutile) in order to investigate the activity for the oxidation of CO. Previous work had associated the activity with ~3 nm sized Au particles and the presence of oxidized Au. However, we found that high activity at low temperatures corresponds to the presence of smaller, ~1 nm, Au particles that are only one or two monolayers thick and fully reduced. Larger (>5 nm) gold particles were far less active. Also, mono-dispersed, single Au atoms were not associated with high activity. First-principles density-functional calculations showed that Au nanoparticles bond only weakly to the stoichiometric anatase (001) surface. Oxygen vacancies in the substrate act as anchors to bond the nanoparticles in place, although at sufficiently high temperatures, the particles can diffuse and coalesce. Using the Au nanoparticle structures seen in the Z-contrast STEM as a starting point, we were able to investigate the catalytic properties. Unlike bulk gold, these nanometer-sized particles are able to adsorb both CO and O_2 molecules. The CO

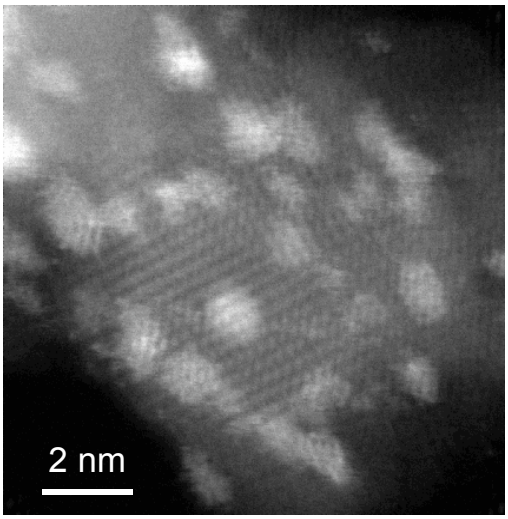

Fig. 3 STEM micrographs of highly active Au / TiO_2 (anatase). Bright patches are Au particles ~ 1nm diameter and mostly one monolayer thick.

adsorbs in an end-on configuration, while the O_2 adsorbs preferentially at the perimeters of the nanoparticles, bonding to both the nanoparticle and the substrate. This suggests that the active sites for O_2 absorption may be at the perimeter of the nanoparticles, explaining the decrease in activity with increasing particle size. In agreement with experiment, single Au atoms adsorbed at vacancies do not bond CO or O_2. (Submitted to Science)

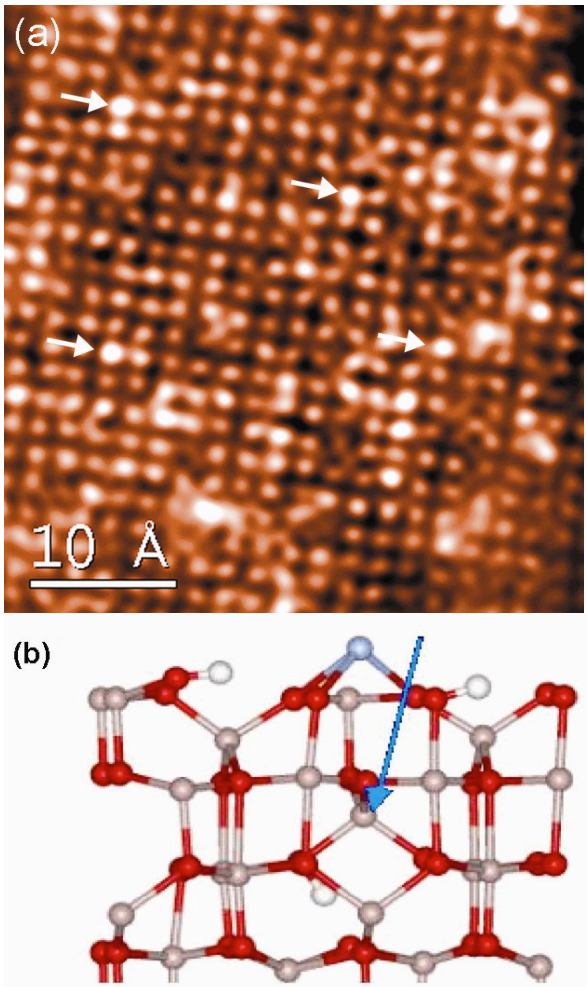

Fig. 2. (a) Z-contrast STEM image of the <100> surface of γ-Al_2O_3: bright spots correspond to La atoms on the surface; several examples of preferred sites are arrowed. (b) calculated lowest-energy configuration of La atom (blue) on the <100> surface of γ-Al_2O_3 above an Al-O column; the Al atom displaced by La is arrowed.

Mechanism of thermal stabilization of γ-Al_2O_3 catalyst supports by La addition: γ-Al_2O_3, a widely used catalytic support material, undergoes an undesirable phase transition to θ-Al_2O_3 at 1000ºC with loss of surface area. Addition of La dopants was previously shown to extend the stability range to 1250ºC, but the mechanism of the stabilization was never determined and was speculated to result from the formation of La_2O_3 or $LaAlO_3$ monolayers on the surface or substitution of Al by La in the bulk. To examine La distribution, samples of La-doped γ-Al_2O_3 were investigated by Z-contrast STEM. It was found that La atoms are distributed on the surface of γ-Al_2O_3 in an uncorrelated fashion; no clusters or ordered monolayers were observed (Fig. 2(a)). On the <100> surface of γ-Al_2O_3 La atoms were found to occupy predominantly the positions directly above Al-O columns (examples arrowed).

Density functional theory calculations, conducted in parallel, have demonstrated that La atoms have overwhelming preference for the surface positions and are very strongly bound to the surface. In full agreement with the microscopic observations, no tendency towards cluster formation was found. The La site on the <100> surface of γ-Al_2O_3 observed by STEM was shown to correspond to the lowest energy configuration (Fig. 2(b)).

The combination of sub-Ångstrom resolution imaging and theory clearly demonstrates that the stabilization is caused by isolated La atoms that bind strongly to

the surface of γ-Al_2O_3, thus pinning it and preventing sintering and phase transformation. (Nature Materials, **3**, 143 (2004)).

DOE Interest

Catalysts are now used at some point in a vast number of modern manufacturing processes, from drug or fuel production to catalytic converters in cars, and will be of increasing importance to the worldwide economy. Understanding how and why they act is greatly assisted by the ability to determine individual cluster configurations.

Future Plans

The newly aberration-corrected STEM provides unique sensitivity for imaging the atomic configurations of supported cluster catalysts, and when combined with reaction rate measurements and density-functional calculations promises significant new insight into many previously unresolved issues, including:

The origin of the synergistic effect of bimetallic catalysts: We presently have the ability to distinguish individual second row transition metals from third row metals, eg. Pt/Ru and Au/Pd. We will investigate the preferred configurations of bimetallic clusters with measured reactivities in collaboration with Profs. M. Amiridis and R. Adams, University of S. Carolina.

Examination of different support materials: In collaboration with other groups we will investigate the role of different support materials, both experimentally, where the single atom-resolved Z-contrast microscopy provides unique insight, and theoretically using DFT calculations.

Three-dimensional imaging: We presently have about a 1 nm depth of view which allows us to image individual atoms with sub-Ångstrom lateral resolution and sub-nm depth resolution. We will investigate techniques for 3D visualization of supported catalyst clusters.

In-situ imaging with 3D atomic resolution: A next generation, aberration-corrected STEM with expected 0.4 Ångstrom lateral and 4 Ångstrom depth resolution has been approved by BES Division of Materials Sciences. This microscope will incorporate an in-situ capability for temperatures up to ~ 800˚C under reaction conditions.

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